

OFFICE OF NAVAL RESEARCH

Grant N00014-95-1-0194
R&T Project 3135008---16

Dr. Kelvin T. Higa

Technical Report No. DU/DC/TR-79

**PREPARATION OF NANOCRYSTALLINE INDIUM ANTIMONIDE
THROUGH β -HYDRIDE ELIMINATION FROM
NEW INDIUM-ANTIMONY SINGLE-SOURCE PRECURSORS**

Edward E. Foos and Richard L. Wells

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University
Durham, NC 27708-0346

and

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, DE 19716

Accepted for Publication in the *Journal of Cluster Science*

Duke University
Department of Chemistry,
P. M. Gross Chemical Laboratory
Box 90346
Durham, NC 27708-0346

22 October 1998

19981027 073

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 22 October 1998		3. REPORT TYPE AND DATES COVERED Technical
4. TITLE AND SUBTITLE PREPARATION OF NANOCRYSTALLINE INDIUM ANTIMONIDE THROUGH β -HYDRIDE ELIMINATION FROM NEW INDIUM-ANTIMONY SINGLE-SOURCE PRECURSORS			5. FUNDING NUMBERS N00014-95-1-0194 R&T Project 3135008---16 Dr. Kelvin T. Higa	
6. AUTHOR(S) E. E. Foos, R. L. Wells and A. L. Rheingold				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Duke University Durham, NC 27708-0346			8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. DU/DC/TR-79	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 300 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Accepted for publication in the <i>Journal of Cluster Science</i>				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The 1:1 mole ratio reaction of $t\text{-Bu}_3\text{In}$ with $\text{Sb}(\text{SiMe}_3)_3$ results in the formation of the Lewis acid-base adduct $t\text{-Bu}_3\text{In}\cdot\text{Sb}(\text{SiMe}_3)_3$ (1), while the dimeric compound $[t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2]_2$ (2) is isolated from the 1:1 reaction of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$. Both the 2:1 reactions of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$ and $t\text{-Bu}_2\text{InCl}$ with 2 result in the formation of the mixed-bridge compound $t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2\text{In}(t\text{-Bu})_2\text{Cl}$ (3), however ^1H NMR studies suggest that this compound is unstable in solution. Thermolysis of 1, 2, and $t\text{-Bu}_3\text{Ga}\cdot\text{Sb}(\text{SiMe}_3)_3$ (4) results in the formation of nanocrystalline InSb or GaSb through a β -hydride elimination pathway.				
14. SUBJECT TERMS nanocrystalline, indium antimonide single-source precursor			15. NUMBER OF PAGES 20	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

**PREPARATION OF NANOCRYSTALLINE INDIUM-ANTIMONIDE THROUGH
 β -HYDRIDE ELIMINATION FROM NEW INDIUM-ANTIMONY SINGLE-
SOURCE PRECURSORS.**

EDWARD E. FOOS AND RICHARD L. WELLS*

Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham,
North Carolina 27708, U.S.A.

ARNOLD L. RHEINGOLD

Department of Chemistry, Drake Hall, University of Delaware,
Newark, Delaware 19716, U.S.A.

*Author for correspondence

Keywords: Nanocrystalline, indium, antimony, precursors.

Abstract- The 1:1 mole ratio reaction of $t\text{-Bu}_3\text{In}$ with $\text{Sb}(\text{SiMe}_3)_3$ results in the formation of the Lewis acid-base adduct $t\text{-Bu}_3\text{In}\cdot\text{Sb}(\text{SiMe}_3)_3$ (**1**), while the dimeric compound $[t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2]_2$ (**2**) is isolated from the 1:1 reaction of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$. Both the 2:1 reactions of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$ and $t\text{-Bu}_2\text{InCl}$ with **2** result in the formation of the mixed-bridge compound $t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2\text{In}(t\text{-Bu})_2\text{Cl}$ (**3**), however ^1H NMR studies suggest that this compound is unstable in solution. Thermolysis of **1**, **2**, and $t\text{-Bu}_3\text{Ga}\cdot\text{Sb}(\text{SiMe}_3)_3$ (**4**) results in the formation of nanocrystalline InSb or GaSb through a β -hydride elimination pathway.

Introduction

Currently, a major area of research in main-group chemistry is the development of single-source precursors to electronic materials. A variety of methods have been employed by ourselves and others in the formation of such compounds, and the bulk of the work has been towards the preparation of nanocrystalline GaN, GaP, GaAs, InP, and InAs [1]. Recently, our focus has been on gallium-nitrogen systems [1, 2] and studying the incorporation of another member of group 15 into our overall effort, namely antimony [3], through the formation and isolation of new potential precursors which have been employed in the exploration of new routes to nanocrystalline materials.

The dehalosilylation reaction has been used widely for the facile formation of 13-15 bonds in potential precursor compounds, as well as for the direct formation of nanocrystalline materials [3b, 4]. This reaction can also be successfully utilized in the gallium-antimony system, as recent investigations have demonstrated [3]. In addition, we

have found that $[t\text{-Bu}_2\text{GaSb}(\text{SiMe}_3)_2]_2$ produces nanocrystalline GaSb under thermolysis conditions through an apparent β -hydride elimination pathway [3a], which involves loss of an alkene followed by a dehydrosilylation step. Based on these results, we were optimistic that these methods could be extended to include the formation of indium-antimony containing precursors and materials, and indeed several such compounds have been reported in the literature [3c, 5]. Of these, only $\text{Me}_2\text{InSb}(t\text{-Bu})_2$ has been successfully utilized as a single-source precursor to InSb [5a]. Interest in nanocrystalline InSb stems from its potential use in high-speed circuits and infrared detectors, a function of its narrow bandgap and high electron mobility [6]. In an effort to further explore the thermolysis behavior of such indium-antimony compounds, herein we report the synthesis and characterization of $t\text{-Bu}_3\text{In}\bullet\text{Sb}(\text{SiMe}_3)_3$ (1), $[t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2]_2$ (2), and $t\text{-Bu}_2\overline{\text{InSb}(\text{SiMe}_3)_2\text{In}(t\text{-Bu})_2\text{Cl}}$ (3), along with their use in the formation of nanocrystalline InSb. Complementary to these studies, we have also examined the thermolysis of the previously reported adduct $t\text{-Bu}_3\text{Ga}\bullet\text{Sb}(\text{SiMe}_3)_3$ (4) [3a].

Experimental Section

General Considerations: All manipulations of air- and moisture-sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by standard Schlenk techniques. Hexane was distilled over sodium/potassium alloy under dry dinitrogen. $t\text{-Bu}_3\text{In}$ [7], $t\text{-Bu}_2\text{InCl}$ [7], and $\text{Sb}(\text{SiMe}_3)_3$ [8] were prepared from literature procedures. InCl_3 was purchased from Strem Chemicals and used as received. The integrity of starting materials, when applicable, was confirmed using ^1H NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Unity XL-400

spectrometer operating at 400 and 100.6 Mhz, respectively. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced to TMS using the residual protons or carbons of deuterated benzene at δ 7.15 or δ 128.0, respectively. All NMR samples were prepared in 5-mm tubes which were septum-sealed under argon. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of $t\text{-Bu}_3\text{In}\cdot\text{Sb}(\text{SiMe}_3)_3$ (1): $t\text{-Bu}_3\text{In}$ (0.429 g, 1.50 mmol) dissolved in hexane was added to a 250 mL round-bottomed flask equipped with a stir bar and Teflon valve. $\text{Sb}(\text{SiMe}_3)_3$ (0.511 g, 1.50 mmol) in hexane was added slowly via pipet and the clear, yellow solution was stirred overnight at room temperature. The volatiles were reduced *in vacuo* and cooled to -30°C to produce clear, colorless crystals of **1** (0.651 g, 70% yield). Anal. Calcd. (found) for $\text{C}_{21}\text{H}_{34}\text{InSbSi}_3$: C, 40.2 (39.97); H, 8.67 (8.59). ^1H NMR: δ 0.39 (s, 27H, $-\text{SiMe}_3$), δ 1.49 (s, 27H, $-\text{CH}_3$). ^{13}C NMR $\{^1\text{H}\}$: δ 4.69 (s, $-\text{SiMe}_3$), δ 34.48 (s, $-\text{CH}_3$).

Thermolysis of 1: **1** (0.651 g, 1.04 mmol) was loaded into a sublimator which was attached to a liquid N_2 cold trap. The sample was heated under static vacuum to 350°C , where the temperature was maintained for 7 hours. A metallic mirror had formed on the inside surface of the sublimator during this time, and was not characterized. 0.03 g of black powder was recovered from the bottom of the sublimator, and identified as InSb through XRD (JCPDS File 6-0208). Elemental In was also present and observed in the pattern (JCPDS File 5-0642). An approximate average particle size of 11 nm was calculated from the XRD data using the Scherrer equation. 1.35 mmol of condensable

gases were trapped during the decomposition, and identified as isobutylene and HSiMe_3 through IR spectroscopy.

Preparation of $[t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2]_2$ (2): $t\text{-Bu}_2\text{InCl}$ (0.264 g, 1.00 mmol) dissolved in hexane was added to a 250 mL round-bottomed flask equipped with a stir-bar and Teflon valve. $\text{Sb}(\text{SiMe}_3)_3$ (0.341 g, 1.00 mmol) dissolved in hexane was added to the flask dropwise via pipet, resulting in a clear, light yellow solution which was stirred overnight at room temperature. During this time, the solution darkened to a green color. The volume was reduced *in vacuo*, and stored at -30°C . Small colorless crystals of **2**, suitable for X-ray analysis were isolated (0.315 g, 63% yield). Anal. Calc. (found) for $\text{C}_{28}\text{H}_{72}\text{In}_2\text{Sb}_2\text{Si}_4$: C, 33.82 (33.66); H, 7.3 (7.23). ^1H NMR: δ 0.59 (s, 36H, $-\text{SiMe}_3$), δ 1.52 (s, 36H, $-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 6.74 (s, $-\text{SiMe}_3$), δ 34.03 (s, $-\text{CH}_3$).

Thermolysis of 2: **2** (0.169 g, 0.34 mmol) was loaded into a sublimator which was attached to a liquid N_2 cold trap, and the sample heated under static vacuum to 200°C . This temperature was maintained for 20 minutes, after which it was ramped to 400°C and held overnight. A metallic mirror formed on the inside surface of the sublimator during this time, and was not characterized. 0.042 g of black powder was recovered from the bottom of the sublimator, and identified as InSb through XRD (JCPDS File 6-0208). Elemental In was also present in the sample and observed in the pattern (JCPDS File 5-0642). An approximate average particle size of 11 nm was calculated using the Scherrer equation. 0.93 mmol of condensable gases were trapped during the decomposition, and identified as isobutylene and HSiMe_3 through IR spectroscopy. Elemental analysis of this sample showed that it contained no carbon or hydrogen. A second sample of InSb was

prepared similar to that described above, and analyzed for In and Sb. Anal. Calc. (found) for InSb: In, 48.54 (54.78); Sb, 51.46 (37.08). In:Sb ratio 1.6:1.

Preparation of $t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2\text{In}(t\text{-Bu})_2\text{Cl}$ (3): (Method 1): **2** (0.267 g, 0.27 mmol) dissolved in hexane was added to a 250 mL round-bottomed flask equipped with a stir-bar and Teflon valve. $t\text{-Bu}_2\text{InCl}$ (0.142 g, 0.54 mmol), also dissolved in hexane, was added dropwise via pipet and the resulting orange solution was allowed to stir for 5 d at room temperature. The volatiles were reduced *in vacuo* and the dark yellow liquid was allowed to evaporate at $-30\text{ }^\circ\text{C}$. Large crystals (0.306 g, 74% yield based on the expected product) formed overnight, and were shown by ^1H NMR to contain $t\text{-Bu}_2\text{InCl}$, **2**, and **3**. ^1H NMR: δ 0.50 (s, 18H, $-\text{SiMe}_3$), δ 1.47 (bs, 36H, $-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 6.45 (s, $-\text{SiMe}_3$), δ 32.53 (s, $-\text{CH}_3$).

(Method 2): The reaction was identical to that described for the formation of **2**. $t\text{-Bu}_2\text{InCl}$ (0.529 g, 2.00 mmol); $\text{Sb}(\text{SiMe}_3)_3$ (0.341 g, 1.00 mmol). ^1H NMR of this sample was identical to that of Method 1.

^1H NMR study of the formation of **3 (Method 2):** $t\text{-Bu}_2\text{InCl}$ (1.5 mg, 0.006 mmol) was added to an NMR tube with $\text{Sb}(\text{SiMe}_3)_3$ (1.0 mg, 0.003 mmol) and approximately 0.6 mL of deuterated benzene. The tube was degassed using several freeze-pump-thaw cycles and then flame sealed. An initial spectra was taken within minutes of mixing, followed by spectra at 1, 2, 3, and 11 d, where no further changes seemed to occur. ^1H NMR (initial): δ 0.16 (s, ClSiMe_3), δ 0.41 (s, $\text{Sb}(\text{SiMe}_3)_3$), δ 0.50 (s, **3**), δ 0.59 (s, **2**), δ 1.38 (s, $t\text{-Bu}_2\text{InCl}$), δ 1.46 (bs, **3**), δ 1.52 (s, **2**). Peaks corresponding to **2** were minor components. ^1H NMR (final): δ 0.16 (s, ClSiMe_3), δ 0.40

(s, $\text{Sb}(\text{SiMe}_3)_3$), δ 0.50 (s, **3**), δ 0.59 (s, **2**), δ 1.30 (s), δ 1.38 (s, $t\text{-Bu}_2\text{InCl}$), δ 1.46 (bs, **3**), δ 1.52 (s, **2**). Peaks corresponding to **3** were minor components.

Thermolysis of $t\text{-Bu}_3\text{Ga}\cdot\text{Sb}(\text{SiMe}_3)_3$ (4**):** **4** (0.112 g, 0.19 mmol) was loaded into a sublimator which was attached to a liquid N_2 cold trap. The sample was heated under static vacuum to 400 °C, where the temperature was maintained overnight. A metallic mirror had formed on the inside surface of the sublimator during this time, and was not characterized. 0.011 g of black powder was recovered from the bottom of the sublimator, and identified as GaSb through XRD (JCPDS File 7-215). An approximate average particle size of 11 nm was calculated using the Scherrer equation. 0.20 mmol of condensable gases were trapped during the decomposition, and identified as isobutylene and HSiMe_3 through IR spectroscopy.

X-ray structural solution and refinement

Crystallographic data for **2** are collected in Table 1, while bond lengths and angles are presented in Table 2. Yellow block crystals were determined to belong to the monoclinic crystal system. Systematic absences in the diffraction data determined that the space group was either $C2/c$ or Cc . Refinement was restricted to the centrosymmetric option in which the ring centroid resides on a crystallographic two-fold axis. An empirical correction for absorption was applied to the data. The structure was solved by direct methods, completed from difference Fourier maps, and refined with anisotropic thermal parameters for all nonhydrogen atoms. All computations used SHELXTL 4.2 and SADABS software (G. Sheldrick, Bruker AXS, Madison, WI).

Results and Discussion

The 1:1 mole ratio reaction of $t\text{-Bu}_3\text{In}$ with $\text{Sb}(\text{SiMe}_3)_3$ affords the Lewis acid-base adduct $t\text{-Bu}_3\text{In}\cdot\text{Sb}(\text{SiMe}_3)_3$ (**1**) in good yield. The isolated crystals of this compound were used for X-ray experiments, however it was not possible to obtain a complete solution due to problems associated with the crystal quality and symmetry [9]. This compound was characterized through NMR and elemental analysis, both of which yielded satisfactory results.

The 1:1 mole ratio reaction of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$ resulted in the isolation of the dimeric compound $[t\text{-Bu}_2\text{InSb}(\text{SiMe}_3)_2]_2$ (**2**). This compound has been fully characterized, including its X-ray crystal structure, and an ORTEP diagram of the structure is shown in Figure 1. Crystals of **2** crystallize in the monoclinic space group $C2/c$. The average indium-antimony bond length of 2.93 Å present in **2** is noticeably longer than the analogous length of 2.88 Å found in the related dimeric compound $[(\text{Me}_3\text{SiCH}_2)_2\text{InSb}(\text{SiMe}_3)_2]_2$ [3c]. Presumably, this is due to the greater steric bulk of the t -butyl groups present in **2**. The average In-Sb-In and Sb-In-Sb endocyclic bond angles in **2** of 95.0° and 85.0°, respectively, compare well with the analogous angles of 95.2° and 84.8° found in $[(\text{Me}_3\text{SiCH}_2)_2\text{InSb}(\text{SiMe}_3)_2]_2$.

In an attempt to isolate a compound in this system containing a mixed-bridge type core ring similar to $t\text{-Bu}_2\text{Ga}\overline{\text{Sb}(\text{SiMe}_3)_2\text{Ga}(t\text{-Bu})_2}\text{Cl}$ [3a], both the 2:1 mole ratio reaction of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$, as well as the reaction of the dimer **2** with two equivalents of $t\text{-Bu}_2\text{InCl}$ were explored. While peaks consistent with the formation of $t\text{-Bu}_2\overline{\text{InSb}(\text{SiMe}_3)_2\text{In}(t\text{-Bu})_2}\text{Cl}$ (**3**) were observed by NMR as a product of both reactions,

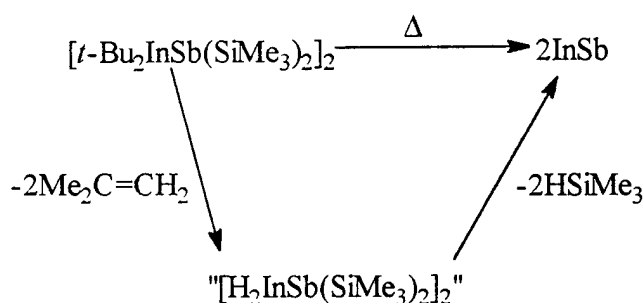
along with significant amounts of **2**, single crystals of **3** could not be isolated. In an attempt to understand the solution behavior of **3**, the 2:1 reaction of $t\text{-Bu}_2\text{InCl}$ with $\text{Sb}(\text{SiMe}_3)_3$ was carried out in an NMR tube, and the reaction monitored at periodic intervals. The first spectra, taken within minutes of mixing the reagents, shows the presence of **3**, in addition to $t\text{-Bu}_2\text{InCl}$, $\text{Sb}(\text{SiMe}_3)_3$, and Me_3SiCl . After 24 hours, peaks corresponding to the dimer **2** were present, along with all other species present in the initial spectra. The ratio of **2**:**3** was approximately 3:1, based on the Me_3Si - protons. This ratio became 6:1 after 48 hours and 11:1 after 72 hours. After 11 days, essentially no **3** was present (**2**:**3** ratio of 20:1). Based on these observations, it seems clear that **3** is unstable in solution, dissociating to the dimer on standing. One new peak also appears in the spectra during the decomposition, at δ 1.30. This peak seems to arise from a secondary product formed during the decomposition and appears in the range expected for an indium bound alkyl group, however it is not feasible to speculate on the structure of the species that gives rise to this new signal.

In order to assess the utility of **1** and **2** as single-source precursors to indium-antimonide, their thermal decomposition behavior was also examined. The related compound $[t\text{-Bu}_2\text{GaSb}(\text{SiMe}_3)_2]_2$ has previously been shown to produce GaSb through a β -hydride elimination pathway [3a], and such behavior was expected in this system as well. An example of such an elimination pathway is shown for **2** in Scheme 1. The synthesis of the adduct $t\text{-Bu}_3\text{Ga}\bullet\text{Sb}(\text{SiMe}_3)_3$ (**4**) was reported in this earlier work, and its thermolysis has now been examined in greater detail. Adducts **1** and **4** were heated to 350 °C and 400 °C, respectively, and exhibited similar thermolysis behavior under these

conditions. Most importantly, both compounds sublimed readily under the conditions of the experiment, indicative of their high volatility. This sublimation is in part responsible for the low yields of bulk material obtained from these thermolysis studies, since an appreciable amount of the precursor moved out of the hot zone of the sublimator and collected on the upper, cooler part of the apparatus. Final yields were 12% for **1** and 30% for **4**. IR analysis of the gases evolved during the decomposition showed that in both cases isobutylene and HSiMe_3 were produced, suggesting a β -hydride elimination pathway. For **1**, the condensed gasses amounted to 22% of the expected total for complete elimination, while in **4** the trapped gasses were 17% of the total. Again, the significant sublimation of these compounds could account for these low values. The materials obtained from the thermolysis of **1** and **4** were identified as InSb and GaSb, respectively, through XRD, and the patterns are shown in Figure 2. The approximate average particle sizes of 11 nm for both the InSb and the GaSb were calculated using the Scherrer equation. In the XRD plot for the InSb obtained from **1**, it can be seen that there is significant contamination from elemental In. Such contamination is also observed (to a lesser degree) in the material isolated from thermolysis of **2**, and its presence can be rationalized on the basis of the observed elimination pathway (*vide infra*). It should also be noted that the peak arising at a 2-Theta angle of approximately 39° (d-spacing of 2.29 Å) can be assigned to both the (220) reflection of InSb as well as the (110) reflection of In. The dimeric compound **2** was found to produce InSb in 53% yield through a β -hydride elimination pathway under similar thermolysis conditions to those described above. Once again, the compound sublimed under the conditions of the experiment,

although to a lesser degree than was observed for the adducts described above. The condensed isobutylene and HSiMe_3 accounted for 67% of the expected total, and the XRD pattern is shown in Figure 2. The average particle size of 11 nm was again calculated using the Scherrer equation. Elemental analysis of several samples of the material produced shows that it is 72% InSb , with a In:Sb ratio of 1.6:1 and essentially no contamination from carbon or hydrogen. The presence of this excess indium can be explained through the suggested β -hydride elimination pathway. In such an elimination, the precursor presumably passes through a transition state where, after elimination of isobutylene, a metal hydride species is present (see Scheme 1). Since stable indium-hydride species are rare, it seems reasonable that some of this intermediate reduces to elemental indium prior to the elimination of trimethylsilane, thus accounting for the observed excess in the final product.

Scheme 1



It is interesting to note that in the indium-antimony system, thermolysis of precursors seems to be the only route to such materials. GaSb has been produced from the direct reaction of GaCl_3 with $\text{Sb}(\text{SiMe}_3)_3$ [3b, 10], however analogous reactions using InCl_3 have only resulted in the isolation of elemental antimony or antimony-oxides (when

ethers were used as reaction solvents) [11]. In the gallium-antimony system, the materials produced through β -hydride elimination from appropriate precursors produce cleaner materials than those isolated from the dehalosilylation reaction of GaCl_3 with $\text{Sb}(\text{SiMe}_3)_3$. In light of these results, such thermolysis pathways merit further investigation, both in this system and in those possibly leading to the isolation of other group 13-pnictides.

Acknowledgment - We wish to thank the Office of Naval Research for their financial support.

Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic temperature factor parameters for **2**. Ordering information is given on any current masthead page.

References

1. See the following and the references contained therein: R. L. Wells and W. L. Gladfelter (1997). *J. Cluster Science* **8**, 217.
2. (a) J. F. Janik, R. L. Wells, J. L. Coffey, J. V. St. John, W. T. Pennington, and G. L. Schimek (1998). *Chem. Mater.* **10**, 1613. (b) J. F. Janik, R. L. Wells (1996). *Chem. Mater.* **8**, 2708.
3. (a) R. L. Wells, E. E. Foos, P. S. White, A. L. Rheingold, and L. M. Liable-Sands (1997). *Organometallics* **16**, 4771. (b) R. A. Baldwin, E. E. Foos, and R. L. Wells (1997). *Mat. Res. Bull.* **32**, 159. (c) R. A. Baldwin, E. E. Foos, R. L. Wells, P. S. White, A. L. Rheingold, and G. P. A. Yap (1996). *Organometallics* **15**, 5035.
4. (a) R. L. Wells, M. F. Self, A. T. McPhail, S. R. Aubuchon, R. C. Woudenberg, and J. P. Jasinski (1993). *Organometallics* **12**, 2832. (b) J. D. Johansen, A. T. McPhail, and R. L. Wells (1992). *Adv. Mater. Opt. Electron.* **1**, 29. (c) R. L. Wells, L. J. Jones, A. T. McPhail, A. Alvanipour (1991). *Organometallics* **10**, 2345.
5. (a) A. H. Cowley, R. A. Jones, C. M. Nunn, and D. L. Westmoreland (1990). *Chem. Mater.* **2**, 221. (b) A. R. Barron, A. H. Cowley, R. A. Jones, C. M. Nunn, and D. L. Westmoreland (1988). *Polyhedron* **7**, 77.
6. J. B. Webb, C. Halpin, and J. P. Noad (1986). *J. Appl. Phys.* **60**, 2949.
7. D. C. Bradley, D. M. Frigo, M. B. Hursthouse, and B. Hussain (1988). *Organometallics* **7**, 1112.

8. E. Amberger and G. Salazar (1967). *J. Organomet. Chem.* **8**, 111.
9. The unit cell parameters for **1** are as follows (triclinic): $a = 11.7459(3)$, $b = 16.1832(4)$, $c = 21.0322(5)$, $\alpha = 99.301(3)$, $\beta = 91.015(2)$, $\gamma = 100.144(3)$.
10. S. Schulz, L. Martinez, and J. L. Ross (1996). *Adv. Mater. Opt. Electron.* **6**, 185.
11. R. L. Wells, and E. E. Foos: *Unpublished Results*.

Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid-state structure and atom numbering scheme for **2**. Hydrogen atoms are omitted for clarity.

Figure 2. XRD plots showing: (a) InSb obtained from the thermolysis of **1** at 350 °C; (b) InSb obtained from the thermolysis of **2** at 400 °C; (c) GaSb obtained from the thermolysis of **4** at 400 °C. Peaks arising from elemental In in (a) and (b) are labeled with an *, while those attributed to InSb are marked with a +.

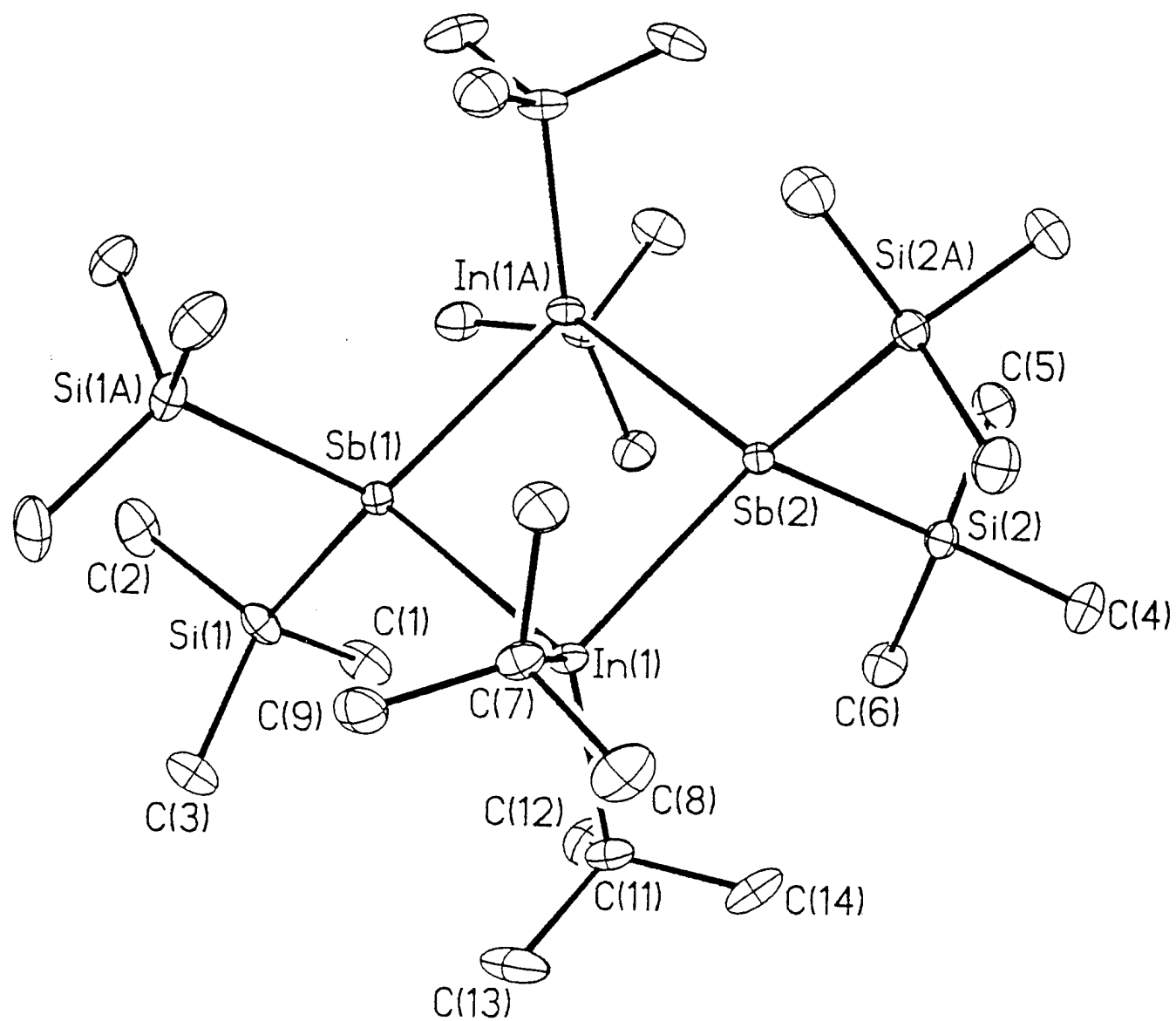


Figure 1.

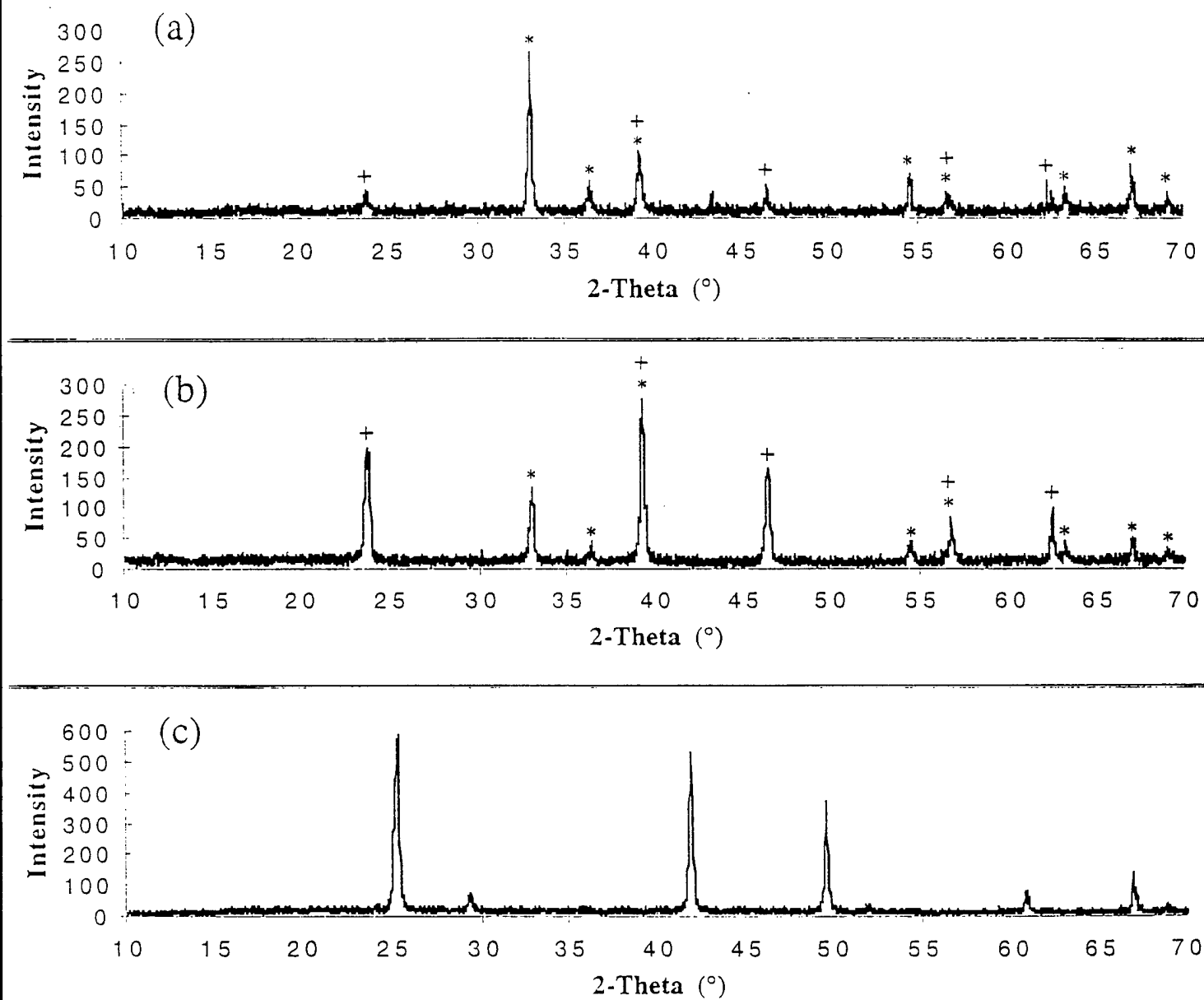


Figure 2.

Table 1. Crystallographic data for [(*t*-Bu)₂InSb(SiMe₃)₂]₂ 2.

formula	C ₂₈ H ₇₂ In ₂ Sb ₂ Si ₄
formula weight	994.36
crystal system	monoclinic
space group	C2/c
<i>a</i> , <i>b</i> , <i>c</i> , Å	20.1764(3), 13.4563(1), 18.7425(3)
<i>β</i> , deg	117.818(1)
volume, Å ³	4500.52(10)
<i>Z</i>	4
<i>D_x</i> , g cm ⁻³	1.468
<i>μ</i> (MoKα), cm ⁻¹	23.2
<i>T</i> , K	173(2)
diffractometer	Siemens P4/CCD (graphite monochromator)
2θ range, deg	4 - 45 (<i>h</i> , -20,24; <i>k</i> , -16,17; <i>l</i> , -23,23)
reflns (collected, independent, observed)	8311, 4309, 3620 (4σ <i>F_o</i>)
<i>R</i> (<i>F</i>), <i>R</i> (<i>wF</i>), ^a %	2.70, 6.72
GOF	1.07
<i>N_o</i> / <i>N_v</i>	26.3

^a *R*(*F*) = ΣΔ/Σ(*F_o*); *R*(*wF*) = Σ[Δ*w*^{1/2}]/[Σ(*F_o**w*^{1/2})]; Δ = |*F_o* - *F_c*|; *w*⁻¹ = σ²(*F_o*) + *gF_o*²

Table 2. Selected bond lengths (Å) and angles (°) for **2** with Estimated Standard Deviations in Parentheses.

Bond Lengths			
In(1)-Sb(1)	2.9273(2)	In(1)-C(11)	2.233(4)
In(1)-Sb(2)	2.9340(2)	Sb(1)-Si(1)	2.5899(8)
In(1)-C(7)	2.232(3)	Sb(2)-Si(2)	2.5925(7)
Bond Angles			
In(1)-Sb(1)-In(1A)	95.116(10)	Sb(1)-In(1)-Sb(2)	85.025(7)
In(1)-Sb(2)-In(1A)	94.833(9)	C(7)-In(1)-Sb(1)	110.36(8)
In(1)-Sb(1)-Si(1)	114.37(2)	C(7)-In(1)-Sb(2)	115.19(8)
In(1)-Sb(1)-Si(1A)	118.40(2)	C(11)-In(1)-Sb(1)	114.65(8)
In(1)-Sb(2)-Si(2)	117.96(2)	C(11)-In(1)-Sb(2)	110.82(8)
In(1)-Sb(2)-Si(2A)	114.75(2)	C(7)-In(1)-C(11)	116.74(13)
Si(1)-Sb(1)-In(1A)	118.40(2)	Si(1A)-Sb(1)-In(1A)	114.37(2)
Si(2)-Sb(2)-In(1A)	114.75(2)	Si(2A)-Sb(2)-In(1A)	117.96(2)
Si(1)-Sb(1)-Si(1A)	97.70(4)	Si(2)-Sb(2)-Si(2A)	98.03(3)

Table 3. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters[$\text{\AA}^2 \times 10^3$] for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij}

tensor.

	x	y	z	$U(\text{eq})$
In(1)	179.9(1)	7574.5(1)	1450.6(1)	21(1)
Sb(1)	0	9042.6(2)	2500	19(1)
Sb(2)	0	6099(1)	2500	19(1)
Si(1)	1088(1)	10309(1)	3143(1)	31(1)
Si(2)	1076(1)	4836(1)	3242(1)	25(1)
C(1)	1970(2)	9735(3)	3943(2)	45(1)
C(2)	826(2)	11351(2)	3635(2)	51(1)
C(3)	1268(2)	10815(2)	2314(2)	43(1)
C(4)	1006(2)	3792(2)	2539(2)	40(1)
C(5)	997(2)	4329(2)	4134(2)	39(1)
C(6)	2026(2)	5412(2)	3609(2)	38(1)
C(7)	-773(2)	7671(2)	204(2)	26(1)
C(8)	-622(2)	6982(3)	-363(2)	47(1)
C(9)	-818(2)	8748(2)	-77(2)	39(1)
C(10)	-1512(2)	7373(2)	181(2)	38(1)
C(11)	1330(2)	7500(2)	1561(2)	33(1)
C(12)	1936(2)	7799(3)	2406(2)	46(1)
C(13)	1375(2)	8201(3)	941(2)	57(1)
C(14)	1449(2)	6426(3)	1376(2)	45(1)

TECHNICAL REPORTS DISTRIBUTION LIST

ORGANOMETALLIC CHEMISTRY FOR ELECTRONIC & OPTICAL MATERIALS

Dr. Kelvin T. Higa
Chemistry Division, 331
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5660

Defense Technical Information
Center (DTIC)
Ft. Belvoir Headquarters Complex
8725 John J. Kingman Road
STE 0944
Ft. Belvoir, VA 22060

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, DC 20375-5320

Dr. John Fischer, Director
Chemistry Division, C0235
Naval Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Richard W. Drisko
Naval Facilities & Engineering
Service Center
Code L52
Port Hueneme, CA 93043

Dr. Eugene C. Fischer
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Bernard E. Douda
Crane Division
Naval Surface Warfare Center
Crane, IN 47522-5000

Dr. Peter Seligman
Naval Command, Control and
Ocean Surveillance Center
RDT&E Division
San Diego, CA 93152-5000

22 October 1998